



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY
LABORATORY

Materials & Molecular Research Division

SEP 10 1981

LIBRARY AND
DOCUMENTS SECTION

Presented at the Flue Gas Desulfurization Symposium,
Morgantown, WV, November 6-7, 1980

THERMODYNAMIC DATA FOR FLUE-GAS DESULFURIZATION PROCESSES

Leo Brewer

August 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782



BL-11758
C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-11758

Thermodynamic Data for Flue-Gas
Desulfurization Processes

Leo Brewer

Materials and Molecular Research Division, Lawrence Berkeley
Laboratory and the Department of Chemistry, University of
California, Berkeley, CA 94720, U.S.A.

Presented at the FGD Symposium, Morgantown, West Virginia,
November 6-7, 1980.

This work was supported by the Assistant Secretary for Fossil Energy,
Office of Coal Research, Advanced Environmental Control Division of the
U.S. Department of Energy under Contract No. W-7405-ENG-48 through the
Morgantown Energy Technology Center, Morgantown, WV.

The efficient design of processes for removal of sulfur dioxide resulting from coal and oil combustion requires thermodynamic and kinetic data for the various materials that might be used in the processes. Examination of the available thermodynamic data for sulfur compounds indicates serious uncertainties and a complete review is planned to provide the best set of internally consistent values obtainable from the literature and from current experiments.

Although the main emphasis will be on information needed for aqueous limestone or lime slurry treatment, the data could also be used for other processes covering a wider temperature range. Thus it is planned to provide the data, when possible, for the range from room temperature to at least 1000K. The present compilation covers most of the materials that might play a role in SO₂ extraction processes and for which data were found. Supplements will be issued as data are obtained for additional substances of interest.

A convenient starting point is the list of recommended values (1) of the report of the CODATA Task Group on key values for thermodynamics, 1977. Some of these values were not considered up-to-date and, as discussed below, appropriate modifications and additions were made to provide what is considered the best set presently available. The present report covers values of ΔH^o₂₉₈, S^o₂₉₈, H^o₂₉₈ - H^o₀, and C^o_P at

298.15K. Values of $-(G^0 - H_{298}^0)/RT$ are tabulated for gases and pure condensed phases to allow extension to higher temperatures. The values tabulated have been divided by R so that the data are in proper form for immediate calculation of the equilibrium constants (2) by $\ln K = -\Delta G^0/RT = -\Delta(G^0 - H_{298}^0)/RT - (\Delta H_{298}^0/R)/T$. As this procedure removes the uncertainty due to R in calculation of heat capacity and entropy values for gases, it was possible to improve the accuracy for some of the atomic species (3). The present compilation, which was prepared for the FGD symposium held at Morgantown, West Virginia on Nov. 6-7, 1980, will be extended to include $-(G^0 - H_{298}^0)/RT$ values for a range of temperature for the aqueous species in a more complete compilation that will be published as part of the proceedings of the FGD symposium at the American Chemical Society meeting in Atlanta, Georgia, held on March 30-31, 1981.

In such a thermodynamic compilation, it is very important to maintain internal consistency. When older data are replaced by more recent data as has been done here, one must ensure that all other values that depended upon the old data have been changed correspondingly. This is difficult to do and the present compilation is only one step in an iterative process that must be carried out continuously to incorporate newer data. The National Bureau of Standards is uniquely equipped to carry out such a process and it is expected that the Bureau will take over the updating of the data that have been presented here.

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environmental Control Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 through the Morgantown Energy Technology Center, Morgantown, WV.

TABLE 1
Thermodynamic Properties of Common Gases at 298.15 K

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_p°/R
O(g)	29 970 ± 10	19.357 ± 0.002	809.2 ± 0.4	2.635
O ₂ (g)	0	24.660 ± 0.004	1 044.1 ± 0.5	3.533
O ₃ (g)	17 100 ± 200	28.733 ± 0.009	1 247 ± 2	4.736
H(g)	26 219 ± 1	13.784 ± 0.001	745.4	2.500
H ₂ (g)	0	15.704 ± 0.004	1 018.5 ± 0.4	3.468
OH(g)	4 700 ± 100	22.086 ± 0.005	1 060 ± 2	3.594
HO ₂ (g)	250 ± 1000	27.54 ± 0.01	1 203 ± 2	4.198
H ₂ O	-29 084 ± 5	22.698 ± 0.005	1 192 ± 1	4.042
H ₂ O ₂	-16 340 ± 30	28.193 ± 0.02	1 342 ± 4	5.099
F(g)	9 548 ± 40	19.080 ± 0.002	783.9 ± 0.5	2.736
F ₂ (g)	0	24.378 ± 0.005	1 061.4 ± 0.5	3.765
HF(g)	-32 870 ± 80	20.887 ± 0.004	1 034.2 ± 0.5	3.504
Cl(g)	14 589 ± 1	19.854 ± 0.002	754.4 ± 0.4	2.627
Cl ₂ (g)	0	26.817 ± 0.005	1 104 ± 1	4.083
HCl(g)	-11 103 ± 16	22.465 ± 0.004	1 039.2 ± 0.5	3.504
Br(g)	13 457 ± 15	21.036 ± 0.002	745.4	2.500
Br ₂ (g)	3 718 ± 13	29.509 ± 0.006	1 170 ± 1	4.337
HBr(g)	-4 376 ± 20	23.884 ± 0.004	1 040.1 ± 0.5	3.505

TABLE I (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_P°/R
I(g)	12 840 ± 2	21.730 ± 0.002	745.4	2.500
I ₂ (g)	7 508 ± 10	31.339 ± 0.008	1 217 ± 3	4.437
HI(g)	3 187 ± 15	24.834 ± 0.005	1 042.2 ± 0.7	3.507
S(g)	33 360 ± 50	20.172 ± 0.004	800.7 ± 0.5	2.847
S ₂ (g)	15 520 ± 80	27.429 ± 0.006	1 098 ± 1	3.909
S ₃ (g)	17 200 ± 400	32.85 ± 0.1	1 400 ± 5	5.78
S ₄ (g)	16 300 ± 400	35.29 ± 0.1	1 720 ± 5	7.93
S ₅ (g)	14 900 ± 400	40.6 ± 0.4	2 210 ± 20	10.73
S ₆ (g)	12 100 ± 400	42.55 ± 0.1	2 700 ± 10	13.54
S ₇ (g)	12 900 ± 400	48.1 ± 0.4	3 160 ± 20	16.1
S ₈ (g)	12 020 ± 180	51.20 ± 0.4	3 740 ± 20	18.71
HS(g)	16 800 ± 600	23.52 ± 0.01	1 100 ± 20	3.90
H ₂ S(g)	-2 470 ± 80	24.735 ± 0.006	1 198 ± 1	4.11
SO(g)	580 ± 50	26.680 ± 0.002	1 055 ± 5	3.625
SO ₂ (g)	-35 700 ± 20	29.841 ± 0.007	1 269 ± 2	4.792
SO ₃ (g)	-47 620 ± 80	30.84 ± 0.01	1 406 ± 2	6.088
SO ₄ (g)	(-37 000) ± 2500			
S ₂ O(g)	-5 400 ± 400	32.10 ± 0.02	1 338 ± 2	5.306
H ₂ SO ₃ (g)	(-64 000) ± 3000	(34.7) ± 1		
H ₂ SO ₄ (g)	-88 300 ± 300	35.9 ± 0.3	1 980 ± 20	10.1

TABLE I (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ} - H_0^{\circ})/R$, K	C_p°/R
H ₂ SO(g)	-(8 000) ± 2000			
H ₂ SO ₂ (g)	-(32 000) ± 2000			
(HO) ₂ S(g)	-(33 700) ± 2500	(35.2) ± 0.5		
HOS(g)	(2 500) ± 2000	(28.7) ± 0.5		
HOSO ₂ (g)	-(49 000) ± 1500	(33.7) ± 0.5		
HOSO ₃ (g)	-(63 000) ± 1000	(36.2) ± 0.5		
HOSO ₄ (g)	-(57 000) ± 2000			
(HO) ₂ S ₂ O ₄ (g)	-(124 000) ± 2500			
(HO) ₂ S ₂ O ₅ (g)	-(142 000) ± 1500			
(HO) ₂ S ₂ O ₆ (g)	-(137 000) ± 1000	(52) ± 1		
N(g)	56 850 ± 50	18.425 ± 0.001	745.4	2.500
N ₂ (g)	0	23.033 ± 0.003	1 042.7 ± 0.1	3.503
NH(g)	42 400 ± 1000	21.783 ± 0.002	1 034.5 ± 0.5	3.511
NH ₂ (g)	23 000 ± 1000	23.439 ± 0.006	1 195 ± 1	4.072
NH ₃ (g)	-5 525 ± 40	23.173 ± 0.01	1 208 ± 1	4.285
NO(g)	10 980 ± 50	25.334 ± 0.002	1 104.0 ± 1	3.592
NO ₂ (g)	4 110 ± 60	28.872 ± 0.004	1 227.7 ± 2	4.472
N ₂ O(g)	9 810 ± 60	26.448 ± 0.002	1 152.3 ± 1	4.646
N ₂ O ₃ (g)	10 420 ± 120	37.84 ± 0.04	2 060 ± 50	8.75
N ₂ O ₄ (g)	1 340 ± 120	36.606 ± 0.01	2 014 ± 4	9.52

TABLE I (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_P°/R
$N_2O_5(g)$	1 600 \pm 180	42.775 \pm 0.8	2 500 \pm 100	11.46
$ONOSO_2(g)$	-23 100 \pm 2000			
$HNO(g)$	12 270 \pm 360	26.557 \pm 0.002	1 196 \pm 1	4.075
H_2NNO_2	-3 100 \pm 1000	32.285 \pm 0.1	1 463 \pm 10	6.78
$HONO(g)$	-9 436 \pm 70	30.544 \pm 0.07	1 395 \pm 5	5.57
$HONO_2(g)$	-16 106 \pm 70	32.09 \pm 0.02	1 430 \pm 10	6.51
$HONH_2(g)$	-6 000 \pm 1000	28.39 \pm 0.3	1 350 \pm 90	5.59
$HO(SO_2)NH_2(g)$	-62 400 \pm 1000			
$HO(SO_2)ONO(g)$	-64 900 \pm 1000			
$HO(SO_2)ONO_2(g)$	-70 000 \pm 1500			
$C(g)$	86 197 \pm 60	19.002 \pm 0.003	786 \pm 1	2.507
$CO(g)$	-13 294 \pm 20	23.761 \pm 0.004	1 043 \pm 1	3.505
$CO_2(g)$	-47 329 \pm 15	25.700 \pm 0.005	1 126 \pm 1	4.466
$CS(g)$	33 460 \pm 300	25.311 \pm 0.005	1 047 \pm 1	3.584
$COS(g)$	-17 090 \pm 200	27.840 \pm 0.004	1 194 \pm 1	4.991
$CS_2(g)$	14 070 \pm 100	28.61 \pm 0.01	1 285 \pm 3	5.492
$CH_4(g)$	-9 000 \pm 40	22.389 \pm 0.005	1 202 \pm 2	4.247
$CH_3OH(g)$	-24 185 \pm 50	28.83 \pm 0.02	1 375 \pm 2	5.30
$CH_2O(g)$	-13 060 \pm 100	26.30 \pm 0.05	1 205 \pm 10	4.26
$HCOOH(g)$	-45 530 \pm 75	29.93 \pm 0.02	1 314 \pm 5	5.494
$(HCOOH)_2(g)$	-98 740 \pm 300	40.01 \pm 0.5	2 360 \pm 100	11.56

TABLE I (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ} - H_0^{\circ})/R$, K	C_p°/R
Mg(g)	17 600 ± 150	17.865 ± 0.001	745.4	2.500
Ca(g)	21 500 ± 150	18.615 ± 0.001	745.4	2.500
Li(g)	19 170 ± 50	16.678 ± 0.002	745.4	2.500
Na(g)	12 880 ± 50	18.475 ± 0.001	745.4	2.500
K(g)	10 730 ± 25	19.271 ± 0.001	745.4	2.500

References to Table I

$O(g)$:(1) except $C_p(8)$; $O_2(g)$:(1,8); $O_3(g)$:(8); $H(g)$: $\Delta H(1)$, rest(3); $H_2(g)$:(1) except $C_p(8)$; $OH(g)$:(8,9); $HO_2(g)$:(8,9); $H_2O(g)$:(1) except $C_p(8,9)$; $H_2O_2(g)$:(8); $F(g)$:(1,8); $F_2(g)$:(1) except $C_p(8)$; $HF(g)$:(1,8); $Cl(g)$, $Cl_2(g)$, and $HC1(g)$:(1) except $C_p(8)$; $Br(g)$: $\Delta H(11)$, rest(3); $Br_2(g)$ and $HBr(g)$:(1) except $C_p(8)$; $I(g)$: $\Delta H(11)$, rest(3); $I_2(g)$:(1) except $C_p(8)$; $HI(g)$:(1,12) except $C_p(8)$; $S(g)$: $\Delta H(13)$, rest(1,8); $S_2(g)$: $\Delta H(10)$, $S_{298}(1,8,9)$, $H_{298}-H_0(9)$, $C_p(8)$ $S_3(g)$ to $S_8(g)$:(8). The calculated S_{298} value (8) for $S_7(g)$ using values for fifteen vibrational frequencies agrees closely with the calculation (15) using new determinations of the vibrational frequencies. However Steudel and Schuster (15) point out that Second law treatment of mass spectrometric data (16,17) yield a higher entropy and they suggest addition of a contribution from pseudorotation. Since the number of degrees of freedom beyond translation and rotation is restricted to fifteen, addition of pseudorotation terms would be offset by removal of vibrational contributions. Although there would be a net increase in entropy, the uncertainty of the temperature coefficients of the mass spectrometric measurements is comparable to the difference between Second and Third law values and no consideration of pseudorotation contributions was considered warranted at this time.

References to Table I (continued)

HS(g), H₂S(g), and SO(g):(8,9); SO₂(g):(1) except C_p(8). The S₂₉₈/R value for SO₂(g) as determined by high-temperature cell measurements (18) is 1.0 lower than the CODATA value (1) and is claimed (18) to be more reliable. However the molecular constants of SO₂ are accurately known (19) and the value calculated using statistical mechanics is much more reliable than the value from cell measurements. SO₃(g):(8); SO₄(g): estimate by (20); S₂O(g):(8); H₂SO₃(g): estimate by (20); H₂SO₄(g):(8,9); H₂SO(g), H₂SO₂(g), HSO(OH)(g), (HO)₂S(g), HOS(g), HOSO₂(g), HSO₃(g), HOSO₄(g), (HO)₂S₂O₄(g), (HO)₂S₂O₅(g), and (HO)₂S₂O₆(g): estimates from (20); N(g):ΔH(1), rest(3); N₂(g):(1,9); NH(g):(8,21); NH₂(g):(8); NH₃(g):(1) except C_p(8); NO(g), NO₂(g), N₂O(g), N₂O₃(g), N₂O₄(g) and N₂O₅(g):(8); ONOSO₂(g): estimate by (20); HNO(g), H₂NNO₂(g), HONO(g), HONO₂(g), and HONH₂(g):(8); HO(SO₂)NH₂(g), HO(SO₂)ONO(g), and HO(SO₂)ONO₂(g): estimates by (20); C(g):(1,9); CO(g) and CO₂(g):(1) except C_p(9); CS(g):(9) except revision of ΔH on basis of (22); COS(g):(9,23); CS₂(g):(9); CH₄(g):(9,23) except ΔH from (24); CH₃OH(g):(25); CH₂O(g):(9) except ΔH from (24); HCOOH(g) and (HCOOH)₂:(26); Mg(g) and Ca(g):(3) with ΔH(10,27); Li(g), Na(g), and K(g):(3) with ΔH(10).

TABLE II

Thermodynamic Properties of Solids and Liquids at 298.15 K

	$\Delta H_{298}^{\circ}/R, \text{ K}$	S_{298}°/R	$(H_{298}^{\circ} - H_0^{\circ})/R, \text{ K}$	C_P°/R
$\text{H}_2\text{O}(\ell)$	-34 378 ± 5	8.413 ± 0.01	1 599 ± 2	9.056
$\text{Br}_2(\ell)$	0	18.307 ± 0.005	2 950 ± 15	9.102
$\text{I}_2(\text{s})$	0	13.968 ± 0.01	1 587 ± 5	6.548
$\text{S}(\text{orthorhombic})$	0	3.855 ± 0.006	530 ± 7	2.730
$\text{H}_2\text{SO}_4(\ell)$	-97 930 ± 20	18.87 ± 0.01	3 396 ± 10	16.67
$\text{HNO}_3(\ell)$	-20 940 ± 60	18.72 ± 0.03	3 285 ± 5	13.215
$\text{NH}_4\text{NO}_3(\text{s})$	-43 980 ± 35	18.18 ± 0.06	2 846 ± 10	16.728
$\text{NH}_4\text{Cl}(\text{s})$	-37 900 ± 30	11.41 ± 0.06	1 887 ± 15	10.11
$(\text{NH}_4)_2\text{SO}_4(\text{s})$	-142 220 ± 60	26.49 ± 0.07	4 252 ± 50	22.55
$\text{NH}_2\text{SO}_2\text{OH}(\text{s})$	-82 500 ± 100			
$\text{C}(\text{graphite})$	0	0.690 ± 0.01	126 ± 2	1.025
$\text{Si}(\text{s})$	0	2.262 ± 0.01	387 ± 1	2.405
$\text{SiO}_2(\alpha \text{ quartz})$	-109 530 ± 120	4.987 ± 0.02	832 ± 2	5.36
$\text{SiO}_2(\alpha \text{ crist.})$	-109 390 ± 150	5.22 ± 0.02	850 ± 4	5.40

TABLE II (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_p°/R
Mg(s)	0	3.93 ± 0.01	601 ± 4	2.994
MgO(s)	-72 340 ± 40	3.24 ± 0.02	620 ± 3	4.46
Mg(OH) ₂ (s)	-111 200 ± 100	7.60 ± 0.025	1 372 ± 3	9.26
MgF ₂ (s)	-135 220 ± 150	6.89 ± 0.05	1 193 ± 5	7.407
MgCl ₂ (s)	-77 500 ± 100	10.77 ± 0.1	1 656 ± 10	8.57
MgCl ₂ ·6H ₂ O(s)	-300 550 ± 100	44.03 ± 0.5	6 710 ± 25	37.97
Mg(OH)Cl(s)	-96 170 ± 200	10.0 ± 1		8.9
MgS(s)	-41 600 ± 1500	6.054 ± 0.05	1 002 ± 5	5.480
MgSO ₃ (s)	-122 080 ± 400	10.4 ± 0.5		
MgSO ₃ ·3H ₂ O(s)	-233 140 ± 400	26 ± 1.5		
MgSO ₃ ·6H ₂ O(s)	-339 700 ± 400	42 ± 2.5		
MgSO ₄ (α)	-154 900 ± 100	11.0 ± 0.1	1 852 ± 10	11.59
MgSO ₄ ·H ₂ O(s)	-193 640 ± 100	15.2 ± 0.5	2 660 ± 50	16.1
MgSO ₄ ·6H ₂ O(s)	-371 580 ± 100	41.9 ± 0.1	6 665 ± 15	41.9
MgSO ₄ ·7H ₂ O(s)	-407 950 ± 80	47.3 ± 0.8	7 470 ± 50	44.8
MgCO ₃ (s)	-131 800 ± 200	7.83 ± 0.03	1 400 ± 4	9.15
MgCO ₃ ·3H ₂ O(s)	-237 790 ± 60	23.53 ± 0.08	3 880 ± 20	28.6

TABLE II (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_P°/R
MgCO ₃ · 5H ₂ O(s)	-308 700 ± 400	33.7 ± 1		
Mg _{3/4} Ca _{1/4} CO ₃ (s)	-136 200 ± 50	9.006 ± 0.04	1 515 ± 6	9.32
Ca(s)	0	5.00 ± 0.05	689 ± 5	3.12
CaO(s)	-76 380 ± 100	4.59 ± 0.04	810 ± 5	5.07
CaO ₂ (s)	-79 600 ± 300	(7.7) ± 0.4		
CaO ₂ · 8H ₂ O(s)	-362 800 ± 500			
Ca(OH) ₂ (s)	-118 400 ± 30	10.015 ± 0.07	1 703 ± 8	10.52
CaF ₂ (s)	-146 800 ± 250	8.23 ± 0.05	1 400 ± 8	8.062
CaCl ₂ (s)	-95 700 ± 120	12.58 ± 0.05	1 858 ± 7	8.73
CaCl ₂ · H ₂ O(s)	-133 450 ± 200	18.9 ± 0.8		
CaCl ₂ · 2H ₂ O(s)	-168 000 ± 150	24.2 ± 1		
CaCl ₂ · 4H ₂ O(s)	-240 300 ± 200	34.7 ± 1.5		
CaCl ₂ · 6H ₂ O(s)	-312 300 ± 150	47.1 ± 0.9		
CaClOH(s)	-109 550 ± 400			
CaS(s)	-57 900 ± 350	6.81 ± 0.15	1 082 ± 15	5.71
CaSO ₃ (s)	-139 400 ± 500	12.18 ± 0.15	1 940 ± 20	10.93
CaSO ₃ · ½H ₂ O(s)	-157 400 ± 300	(14.7) ± 0.2	(2 300) ± 100	(14.0)

TABLE II (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_P°/R
CaSO_4 (anhydride)	-172 500 ± 40	12.82 ± 0.07	2 070 ± 20	11.987
CaSO_4 (sol. α)	-171 430 ± 50	13.03 ± 0.1	2 096 ± 20	12.05
CaSO_4 (sol. β)	-170 900 ± 50	13.03 ± 0.1	2 091 ± 20	11.91
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (α)	-189 650 ± 50	15.70 ± 0.1	2 480 ± 15	14.36
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (β)	-189 400 ± 50	16.15 ± 0.1	2 544 ± 15	14.93
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (s)	-243 280 ± 40	23.33 ± 0.07	3 750 ± 20	22.3
$\text{CaS}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (s)	-348 430 ± 500			
$\text{Ca}(\text{NO}_2)_2$ (s)	-89 520 ± 100	(19.8) ± 0.5		
$\text{Ca}(\text{NO}_3)_2$ (s)	-112 840 ± 50	23.25 ± 0.09	3 420 ± 35	17.97
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (s)	-185 330 ± 130	32.7 ± 1.5		
$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (s)	-220 200 ± 170	37.7 ± 2		
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (s)	-256 530 ± 140	42.8 ± 2.5		
CaCO_3 (calcite)	-144 920 ± 50	10.03 ± 0.04	1 740 ± 10	10.04
$\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (s)	-179 830 ± 100	15.807 ± 0.03		
$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (s)	-356 200 ± 200	40.214 ± 0.07		
Li (s)	0	3.50 ± 0.02	557 ± 5	2.978
LiOH (s)	-58 625 ± 25	5.15 ± 0.06	892 ± 4	5.965

TABLE II (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ} - H_0^{\circ})/R$, K	C_p°/R
LiOH·H ₂ O(s)	-95 030 ± 25	8.61 ± 0.06	1 461	9.56
LiF(s)	-74 360 ± 40	4.32 ± 0.07	778 ± 3	5.03
LiCl(s)	-49 155 ± 25	7.11 ± 0.06	1 119 ± 3	5.776
Li ₂ SO ₄ (s)	-172 790 ± 45	13.71 ± 0.07	2 240 ± 5	14.145
Na(s)	0	6.17 ± 0.02	777 ± 2	3.397
NaOH(s)	-51 232 ± 20	7.79 ± 0.06	1 260 ± 4	7.16
NaOH·H ₂ O(s)	-88 370 ± 25	11.93 ± 0.06	1 875 ± 5	10.844
NaF(s)	-69 345 ± 40	6.16 ± 0.07	1 021 ± 5	5.635
NaCl(s)	-49 470 ± 20	8.66 ± 0.06	1 276 ± 4	6.075
Na ₂ S(s)	-44 000 ± 1500	11.6 ± 2		9.96
Na ₂ SO ₄ (s)	-166 930 ± 40	17.99 ± 0.06	2 790 ± 4	15.308
Na ₂ SO ₄ ·10H ₂ O(s)	-520 560 ± 40	71.15 ± 0.06		69.09
NaNO ₃ (s)	-56 240 ± 30	13.97 ± 0.06	2 071 ± 5	11.19
Na ₂ CO ₃ (s)	-135 820 ± 30	16.23 ± 0.1	2 503 ± 5	13.29
Na ₂ CO ₃ ·H ₂ O(s)	-171 960 ± 30	20.22 ± 0.1	3 168 ± 5	17.51
Na ₂ CO ₃ ·7H ₂ O(s)	-384 700 ± 50	51.3 ± 0.2		
NaHCO ₃ (s)	-114 130 ± 25	12.33 ± 0.15	1 917 ± 4	10.54
NaCHO ₂ (s)	-80 160 ± 50	12.48 ± 0.1	1 896 ± 5	9.94

TABLE II (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	$(H_{298}^{\circ}-H_0^{\circ})/R$, K	C_P°/R
K(s)	0	7.78 ± 0.02	852 ± 2	3.558
KF(s)	-68 520 ± 40	8.00 ± 0.07	1 203 ± 5	5.90
KF·2H ₂ O(s)	-140 245 ± 40	18.6 ± 0.2		
KCl(s)	-52 473 ± 20	9.97 ± 0.06	1 364 ± 3	6.17
K ₂ SO ₄ (s)	-172 900 ± 50	21.12 ± 0.07	3 059 ± 5	15.98
K ₂ S ₄ O ₆ (s)	-215 900 ± 600	37.244 ± 0.04	5 266 ± 5	27.76
KNO ₃ (s)	-59 395 ± 30	16.00 ± 0.06	2 258 ± 4	11.58

References to Table II

$H_2O(l)$: (1) except $C_p(9)$; $Br_2(l)$ and $I_2(s)$: (1) except $C_p(8)$;
 S (orthorhombic): (1) except $C_p(8,9)$, $H_2SO_4(l)$: ΔH and $S(28)$,
rest (9, 27, 29); $HNO_3(l)$: (23, 27); $NH_4NO_3(s)$: (8, 30); $NH_4Cl(s)$
and $(NH_4)_2SO_4(s)$: ΔH , $S(30)$, rest (27); $NH_2SO_2OH(s)$: (31);
 C (graphite): (1, 9, 23); $Si(s)$: (1) except $C_p(23,27)$; SiO_2
(α quartz): (1) except $C_p(9,27)$; SiO_2 (cristobalite): $\Delta H(32)$,
rest (33); $Mg(s)$: (1) except $C_p(10)$; $MgO(s)$: (1) except C_p
(9, 27); $Mg(OH)_2(s)$: (27, 29); $MgF_2(s)$: (1, 9); $MgCl_2(s)$: $\Delta H(34)$,
rest (27, 9); $MgCl_2 \cdot 6H_2O(s)$, $Mg(OH)Cl(s)$: (27), and $MgS(s)$: (9, 57);
 $MgSO_3(s)$, $MgSO_3 \cdot 3H_2O(s)$, and $MgSO_3 \cdot 6H_2O(s)$: (27); α $MgSO_4(s)$
and $MgSO_4 \cdot H_2O(s)$: (27, 76); $MgSO_4 \cdot 6H_2O(s)$ and $MgSO_4 \cdot 7H_2O$: (27).

$MgCO_3(s)$,
 $MgCO_3 \cdot 3H_2O(s)$, and $MgCO_3 \cdot 5H_2O(s)$: (27, 35); $Mg_{3/4}Ca_{1/4}CO_3(s)$: (35);
 $Ca(s)$ and $CaO(s)$: (1, 9); $CaO_2(s)$ and $CaO_2 \cdot 8H_2O(s)$:
(27); $Ca(OH)_2(s)$: ΔH and S (28), rest (9); $CaF_2(s)$, $CaCl_2(s)$
and its hydrates, $CaClOH(s)$, and $CaS(s)$: (27); $CaSO_3$: (36)
except $H_{298}-H_0$ (27); $CaSO_3 \cdot \frac{1}{2}H_2O(s)$: (37); $CaSO_4$ and its hydrates:
(38); $CaS_2O_3 \cdot 4H_2O(s)$ and $Ca(NO_2)_2(s)$: (27); $Ca(NO_3)_2(s)$: ΔH
and S (28), rest (27); $Ca(NO_3)_2$ hydrates: (27) with addition
of 68K to $\Delta H/R$ values to be consistent with Table III; $CaCO_3$
(calcite): $\Delta H(28)$, rest (39); $CaCO_3$ hydrates: (27) with addition
of 233K to $\Delta H/R$ values to be consistent with calcite value;

References to Table II (continued)

Li(s):(1) except C_p (10); LiOH(s), LiOH·H₂O(s), LiF(s) and
LiCl(s): ΔH and S (30), rest (9); Li₂SO₄(s):ΔH;ΔS(28), rest (9);
Na(s):(1) except C_p (40); NaOH(s), NaOH·H₂O(s), NaF(s), and
NaCl(s):(30) except H₂₉₈-H₀ and C_p from (9); Na₂S:(9);
Na₂SO₄(s) and Na₂SO₄·10H₂O(s):ΔH, S(30) with rest (9,41);
NaNO₃(s):(30) except C_p (57); Na₂CO₃(s):ΔH, S(28,42), rest
(9,41); Na₂CO₃(s)·H₂O(s):(42); Na₂CO₃·7H₂O(s):(40) corrected
to agree with (28) and (42) for the other carbonates; NaHCO₃(s):
(42) except C_p (57); NaCHO₂(s):(40); K(s):(1) except C_p (40,57);
KF(s):(9,30,40); KF·H₂O(s):(28); KC1(s) and K₂SO₄(s):ΔH and S (30),
rest (9,41); K₂S₄O₆(s):(37); KNO₃(s):(30) except C_p (57).

TABLE III

Thermodynamic Properties of Aqueous Species at 298.15 K (m/kg for all species)

	$\Delta H_{298}^{\circ}/R, \text{ K}$	S_{298}°/R	C_P°/R
H ₂ (aq)	-486 ± 100	6.9 ± 0.3	21 ± 3
O ₂ (aq)	-1 460 ± 25	13.1 ± 0.1	27 ± 3
O ₃ (aq)	15 100 ± 300	17.8 ± 1	
H ₂ O(l)	-34 378 ± 5	8.413 ± 0.01	9.056
H	0	0	0
OH ⁻	-27 666 ± 5	-1.305 ± 0.02	-16.9 ± 0.4
H ₂ O ₂ (aq)	-22 990 ± 10	17.51 ± 0.03	
HO ₂ ⁻	-19 280 ± 200	2.87 ± 0.5	
O ₂ ⁼	(-4 500) ± 1500	(-5) ± 5	
HO ₂ ⁻ (aq)	-6 400 ± 1000	17 ± 2	
O ₂ ⁻	-6 400 ± 1000	5 ± 4	
OH(aq)	-600 ± 300	7.8 ± 1	
O ⁻	4 500 ± 1000	-2 ± 2	(-14) ± 3
F ⁻	-40 334 ± 80	-1.67 ± 0.10	-14.1 ± 0.5
Cl ₂ (aq)	-2 500 ± 500	16 ± 1	-10 ± 5
Cl ⁻	-20 095 ± 10	6.81 ± 0.02	-15.1 ± 0.5
Br ₂ (aq)	-260 ± 100	15.7 ± 0.2	

TABLE III (CONTINUED)

	$\Delta H_{298}^0/R$, K	S_{298}^0/R	C_p^0/R
Br ⁻	-14 600 ± 20	9.95 ± 0.02	-15.9 ± 0.5
I ₂ (aq)	2 700 ± 50	16.4 ± 0.2	35 ± 4
I ⁻	-6 830 ± 10	12.80 ± 0.02	-14.5 ± 0.5
I ₃ ⁻	-6 300 ± 50	28.5 ± 0.2	0 ± 5
H ₂ S(aq)	-4 600 ± 120	15.3 ± 0.4	24 ± 1
HS ⁻	-1 800 ± 120	8.5 ± 0.5	-10 ± 3
S ⁼	4 000 ± 2000	-11 ± 5	
H ₂ S ₂ (aq)	(-6 300) ± 1500	(20) ± 3	
HS ₂ ⁻	(-2 950) ± 1500	(12) ± 3	
S ₂ ⁼	3 600 ± 1500	(-2) ± 5	
H ₂ S ₃ (aq)	(-4 800) ± 1500	(24) ± 3	
HS ₃ ⁻	(-1 950) ± 1500	(16) ± 3	
S ₃ ⁼	3 100 ± 1500	(4) ± 5	
H ₂ S ₄ (aq)	-4 200 ± 400	(28) ± 3	
HS ₄ ⁻	-1 650 ± 400	(20) ± 3	
S ₄ ⁼	2 600 ± 400	12.4 ± 5	
H ₂ S ₅ (aq)	-3 450 ± 500	(32) ± 2	
HS ₅ ⁻	-1 100 ± 500	(24) ± 2	
S ₅ ⁼	2 750 ± 500	17 ± 5	
S ₆ ⁼	2 850 ± 500	(22) ± 5	

TABLE III (CONTINUED)

	$\Delta H_{298}^{\circ}/R, \text{ K}$	S_{298}°/R	C_p°/R
$\text{SO}_2(\text{aq})$	-38 670 \pm 100	20.1 \pm 0.4	13.6 \pm 2
$\text{H}_2\text{SO}_3(\text{aq})$	-73 050 \pm 100	28.5 \pm 0.4	22.7 \pm 2
HSO_3^-	-76 000 \pm 150	14.4 \pm 0.5	(0) \pm 4
$\text{S}_2\text{O}_5^{=}$	-118 200 \pm 600	15 \pm 2	
SO_3^-	-76 640 \pm 450	-4.2 \pm 1.5	-40 \pm 5
HSO_4^-	-106 560 \pm 200	16.2 \pm 0.15	-10 \pm 6
$\text{SO}_4^{=}$	-109 380 \pm 60	2.2 \pm 0.1	-33.4 \pm 0.8
$\text{H}_2\text{S}_2\text{O}_3(\text{aq})$	-73 150 \pm 450	(30) \pm 3	
HS_2O_3^-	-76 300 \pm 400	(18) \pm 3	
$\text{S}_2\text{O}_3^{=}$	-79 300 \pm 360	4 \pm 1	-30 \pm 1
$\text{S}_2\text{O}_4^{=}$	-90 630 \pm 2000	11 \pm 2	
$\text{S}_2\text{O}_6^{=}$	-144 100 \pm 2000	13.4 \pm 3	
$\text{S}_2\text{O}_7^{=}$	-168 500 \pm 2000	(24) \pm 3	
$\text{S}_2\text{O}_8^{=}$	-161 700 \pm 1000	29.4 \pm 2	-13 \pm 1
$\text{S}_3\text{O}_6^{=}$	-144 300 \pm 2000	(30) \pm 3	
$\text{S}_4\text{O}_6^{=}$	-148 700 \pm 800	31.3 \pm 0.2	-6.1 \pm 1.5
$\text{S}_5\text{O}_6^{=}$	-148 700 \pm 2000	(33) \pm 3	

TABLE III (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	C_p°/R
N_2 (aq)	-1 255 \pm 100	11.5 \pm 0.3	29.6
NH_3 (aq)	-9 780 \pm 25	13.39 \pm 0.1	9.0 \pm 0.4
NH_4OH (aq)	-44 160 \pm 25	21.80 \pm 0.1	18.1 \pm 0.4
NH_4^+	-16 030 \pm 30	13.37 \pm 0.05	8.3 \pm 0.5
NH_2OH (aq)	-11 800 \pm 400	19.5 \pm 1	
NH_3OH^+	-16 070 \pm 400	18.6 \pm 0.8	
N_2H_4 (aq)	4 130 \pm 20	(16.6) \pm 1	
$N_2H_5^+$	-910 \pm 100	18 \pm 1	8.45 \pm 2
HNO_2 (aq)	-14 300 \pm 100	16.3 \pm 1	
NO_2^-	-12 590 \pm 100	14.8 \pm 0.5	-11 \pm 3
NO_3^-	-24 880 \pm 50	17.63 \pm 0.05	-8.7 \pm 0.5
$H_2N_2O_2$ (aq)	-7 700 \pm 400	26 \pm 1	
HN_2O_2	-6 250 \pm 800	17 \pm 1	
$N_2O_2^=$	-2 070 \pm 800	3 \pm 2	
N_2O (aq)	7 200 \pm 300	14.1 \pm 1	22 \pm 5
NO(aq)	9 550 \pm 300	14.3 \pm 1	26 \pm 5

TABLE III (CONTINUED)

	$\Delta H_{298}^{\circ}/R$, K	S_{298}°/R	C_p°/R
HCN(aq)	12 880 \pm 100	15.3 \pm 0.3	
CN ⁻	18 110 \pm 100	11.6 \pm 0.3	
HCNO(aq)	-18 800 \pm 200	16.1 \pm 1	
CNO ⁻	-17 550 \pm 70	12.28 \pm 0.5	
HCNS(aq)	11 150 \pm 300	(22) \pm 1	
CNS ⁻	9 190 \pm 300	17.36 \pm 0.2	-4.8 \pm 2
CO ₂ (aq)	-49 704 \pm 25	14.36 \pm 0.07	25.5 \pm 2
H ₂ CO ₃ (aq)	-84 080 \pm 25	22.77 \pm 0.07	34.5 \pm 2
HCO ₃ ⁼	-82 980 \pm 20	11.84 \pm 0.07	-6.5 \pm 0.5
CO ₃ ⁼	-81 210 \pm 30	-6.01 \pm 0.1	-32.9 \pm 0.5
CO(aq)	-14 630 \pm 60	12.3 \pm 0.2	27 \pm 3
H ₂ CO(aq)	-17 300 \pm 700	13.3 \pm 2	
H ₂ C(OH) ₂ (aq)	-55 200 \pm 700	17.7 \pm 2	
H ₂ COOH	-47 600 \pm 1500	11. \pm 3	
HCOOH(aq)	-51 200 \pm 50	19.7 \pm 0.5	-10 \pm 4
HCOO ⁻	-51 220 \pm 50	11.0 \pm 0.5	-10.6 \pm 1

TABLE III (CONTINUED)

	$\Delta H_{298}^{\circ}/R, \text{ K}$	S_{298}°/R	C_p°/R
$\text{CH}_3\text{COOH}(\text{aq})$	-58 410 ± 50	21.5 ± 0.3	20.4 ± 0.3
CH_3COO^-	-58 454 ± 50	10.4 ± 0.3	3.2 ± 0.3
$(\text{COOH})_2(\text{aq})$	-98 040 ± 100	22.5 ± 0.3	
$\text{C}_2\text{O}_4^{\text{H}^-}$	-98 440 ± 100	18.0 ± 0.3	
$\text{C}_2\text{O}_4^{\text{H}}$	-99 250 ± 100	5.49 ± 0.3	
$(\text{CH}_2)_2(\text{COOH})_2(\text{aq})$	-109 665 ± 10	(30) ± 2	27.1 ± 0.5
$(\text{CH}_2)_2(\text{COO})_2^{\text{H}^-}$	-109 260 ± 20	(21.65) ± 2	
$(\text{CH}_2)_2(\text{COO})_2^{\text{H}}$	-109 200 ± 20	(8.8) ± 2	
$(\text{CH}_2)_4(\text{COOH})_2(\text{aq})$	-104 000 ± 1000	(38) ± 2	40.4 ± 1
$(\text{CH}_2)_4(\text{COO})_2^{\text{H}^-}$	-104 200 ± 1000	(27.15) ± 2	
$(\text{CH}_2)_4(\text{COO})_2^{\text{H}}$	-104 520 ± 1000	(13.6) ± 2	
Mn^{++}	-26 600 ± 150	-8.15	-1.3 ± 0.4
Mn^{+++}	(-14 000) ± 900		
Fe^{++}	-10 700 ± 100	-16.6 ± 0.3	-0.5 ± 4
Fe^{+++}	-5 840 ± 100	-38 ± 0.5	
Mg^{++}	-56 100 ± 130	-16.6 ± 0.2	-1.9 ± 1
Ca^{++}	-65 270 ± 400	-6.74 ± 0.1	-3.6 ± 1
Li^+	-33 498 ± 10	1.48 ± 0.1	7.3 ± 0.5
Na^+	-28 912 ± 10	7.03 ± 0.02	5.1 ± 0.5
K^+	-30 322 ± 10	12.17 ± 0.02	1.6 ± 0.5

References to Table III

H_2 (aq), O_2 (aq), and O_3 (aq): (43); $H_2O(l)$: (1) except $C_p(9)$; OH^- : ΔH (1), $S(28)$, $C_p(44,59)$; H_2O_2 (aq) and HO_2^- (23); O_2^- : The Brønsted and Calvin equation (66) was used to calculate the ionization constant of HO_2^- and the entropy of ionization was estimated. HO_2^- (aq), $HO_2^{\overset{O^-}{\wedge}}$ (aq), and O^- : Baxendale, Ward, and Wardman (67) have reviewed earlier measurements of the ionization constants of HO_2^- and OH and have carried out measurements over a range of temperature to obtain the enthalpies and entropies of ionization. They suggested that the enthalpies and entropies of solution would be closely the same for $H_2O_2(g)$ and $HO_2(g)$ and also for $H_2O(g)$ and $OH(g)$. Their suggested procedure was used with the data from Tables I and III to calculate the values tabulated in Table III for HO_2^- (aq) and OH (aq). Their ionization data were then used to obtain the values for O_2^- and O^- . Their ΔG° and ΔH° values for the ionization of OH were shifted slightly to increase S°/R of O^- from -3 to -2 to better match the value for F^- . The solvation enthalpies of O^- and F^- are almost the same and C_p for O^- was approximated by the value for F^- . F^- : $\Delta H(1)$, $S(28)$, $C_p(45)$; Cl^- : $\Delta H(1)$, $S(28)$, $C_p(46,59)$; Br_2 (aq): Wu et al. (47) treated the solubility of $Br_2(l)$ in water as a function of temperature with a correction for deviation from Henry's law to obtain thermodynamic values for Br_2 (aq). The difference between their values and the later evaluation of Vasil'ev et al. (48) corresponds to $\ln \gamma_{Br_2} = -(0.689 + 735/T)m$ or $\gamma_{Br_2} = 0.5$ for $m_{Br_2} = 0.22M$ at 298K which

References to Table III (continued)

seems to be too rapid a deviation from Henry's law. The deviation was reduced to $\ln \gamma_{Br_2} = -0.4m$ yielding $\Delta H_{298}^0/R = -260 \pm 100K$ and $\Delta S_{298}^0/R = -2.6 \pm 0.2$ for $Br_2(l) = Br_2(aq)$. Br^- : (28) except C_p (49); $I_2(aq)$: (47,50); I^- : (12) and (28) except C_p (45); I_3^- : Ramette and Sandford (50) have shown that I_5^- and $I_6^{=}$ formation causes errors in the evaluation of thermodynamic values for I_3^- using either I_2 solubility in I^- solutions or calorimetric data with substantial I_2 and I_3^- activities. Johnson (12) has confirmed this effect by demonstrating that the molal enthalpy of solution of I_2 in $HI(aq)$ varies with the amount of I_2 added. The solubility, calorimetric, and spectral measurements have been weighted with regard to influence of I_5^- and $I_6^{=}$ to obtain the values of Table III. $H_2S(aq)$: There have been a number of recent reviews of the solubility of H_2S in water as a function of temperature (43,51,52). The CODATA review (53) has also used calorimetric data to obtain recommended thermodynamic

References to Table III (continued)

values, but their values yield solubilities as much as 13% low between 40 and 260°C. If $\Delta H_{298}^0/R$ for solution of H_2S is made 200K more positive, a good fit is obtained but this appears to be too large a shift from the calorimetric determinations and the CODATA $\Delta H_{298}^0/R$ value was made only 95K more positive to obtain the values of Table III. HS: In addition to the data considered by CODATA (53), the determination of the first ionization constant of H_2S up to 150°C by Tsonopoulos et al. (54) and the calorimetric measurements by Jordan (55) were used. As noted below in the S^- discussion, the tentative second ionization constant accepted by CODATA is believed to be too large by several orders of magnitude and the correction they applied to calorimetric data for hydrolysis of HS^- to S^- would be too large. The tentative CODATA values yield for $OH^- + H_2S(g) = HS^- + H_2O$, $\Delta H_{298}^0/R = -6250K$. Jordan (55) has measured the enthalpy of solution of $H_2S(g)$ in 0.1M NaOH and in 0.2M ammonia buffer solutions and has obtained values corresponding to the OH^- reaction between -5890 and -5850K. The dilution correction should be small for this reaction. These values would appear to confirm that the CODATA values for the enthalpy of solution of H_2S and for the first ionization of H_2S should be more positive. As noted above, the CODATA value for the enthalpy of solution was made 95K more positive. The ionization enthalpy was made more positive by 110K resulting in a compromise between the Jordan and CODATA values of $-6040 \pm 120K$.

References to Table III (continued)

S^{\pm} : The CODATA review (53) notes that reported values of the second ionization constant of H_2S range almost eight orders of magnitude. They selected a tentative value of $\log K_2 = -13$. However, Giggenbach (56) has clearly shown that the ready oxidation of HS^- solutions to polysulfide species has invalidated previous measurements; he demonstrated that $\log K_2$ is at least 1.2 more negative than $\log K$ for the ionization of water at all temperatures and is of the order of -17 at $25^{\circ}C$.

Tsonopoulos et al. (54) report identical pH titration curves for 0.1M HCl with 0.28M Na_2S or with NaOH. Thus the hydrolysis of S^{\pm} must be very complete. They suggest $K_2 = 2 \times 10^{-16}$, but with the S^{\pm} concentration so small, they can only set a limit. A value of $\log K_2 = -17 \pm 2$ is used for Table III. The enthalpy and entropy values suggested by Giggenbach were made somewhat more positive. It should be noted that changes in $K_1 K_2$ or changes in ΔG° and ΔH° of S^{\pm} can be disastrous in calculating the solubilities of metal sulfides if the K_{SP} values are not made consistent with the value of $K_1 K_2$ selected. Whenever $K_1 K_2$ is increased by a factor q , the old value of K_{SP} must be divided by q to maintain the same equilibrium constant or ΔG° for $MS(s) + 2H^+ = M^{++} + H_2S(g)$. An additional confirmation of the value selected for K_2 of H_2S is given by the recent work of Meyer and Peter (60). They examined the Raman spectrum of HS^- in oxygen-free 1M NaOH and in a solution saturated with solid NaOH. Equal amounts of Na_2S had been added to each

References to Table III (continued)

solution. The HS^- intensity was the same within experimental error in both solutions indicating complete hydrolysis even in a saturated NaOH solution and confirming a pK of at least 17.

The ΔH values given by the NBS (23) for S_2^{\pm} and S_3^{\pm} were accepted. They are presumably based on the work of Maronny (62). The NBS entropies for S_4^{\pm} and S_5^{\pm} were also accepted. The remainder of the entropy and enthalpy of formation values were estimated to be consistent with the equilibrium measurements of Schwarzenbach and Fischer (61) for HS_4^- , HS_5^- , and their ions and with their estimates for HS_2^- , HS_3^- , and their ions and the measurements of Boulegue and Michard⁽⁷²⁾ on S_4^{\pm} , S_5^{\pm} , and S_6^{\pm} . The ΔH values for S_2^{\pm} and S_3^{\pm} were given a large uncertainty as Schwarzenbach and Fischer report that S_2^{\pm} and S_3^{\pm} are not detectable in solution and they discredit the cell measurements of Maronny.

$\text{SO}_2(\text{aq})$, $\text{H}_2\text{SO}_3(\text{aq})$: (52); HSO_3^- : Measurements of the ionization constant of sulfurous acid have grouped around 0.017 and 0.013. On the basis of the work of Huss and Eckert (63), 0.014 ± 0.001 was accepted and the thermodynamic values given by Cobble et al. (37) have been revised. Various estimates of C_p^0 of HSO_3^- vary from negative to positive; $C_p^0/R = 0 \pm 4$ seems to be the best estimate available at the moment. $\text{S}_2\text{O}_5^{\pm}$: (64); SO_3^{\pm} : (37), the calorimetric determination of the enthalpy of formation of SO_3^{\pm} was given preference to the temperature coefficient of the ionization constant between 5 and 50°C (68); HSO_4^- , SO_4^{\pm} : (1, 28, 65) except C_p of SO_4^{\pm} (45, 73, 74, 75).

References to Table III (continued)

$\text{H}_2\text{S}_2\text{O}_3$ (aq), HS_2O_3^- : Ionization constants (71) were combined with $\text{S}_2\text{O}_3^{\equiv}$ value of Cobble et al. (37); C_p of $\text{S}_2\text{O}_3^{\equiv}$ (73). $\text{S}_2\text{O}_4^{\equiv}$, $\text{S}_2\text{O}_6^{\equiv}$, $\text{S}_2\text{O}_7^{\equiv}$, $\text{S}_2\text{O}_8^{\equiv}$, $\text{S}_3\text{O}_6^{\equiv}$: (40); C_p of $\text{S}_2\text{O}_8^{\equiv}$ (73). $\text{S}_4\text{O}_6^{\equiv}$: (37) except for correction of arithmetical error in ΔH calculation. $\text{S}_5\text{O}_6^{\equiv}$: (27, 40).

N_2 (aq): (43); NH_3 (aq), NH_4OH (aq), and NH_4^+ : New measurements and reviews of earlier values have been presented recently (77-80). The values in Table III are based on the CODATA selections (1, 28) for ΔH_{298}° and S_{298}° of NH_4^+ with C_p (46, 77); NH_2OH (aq) and NH_3OH^+ : (23, 82, 83); N_2H_4 (aq) and N_2H_5^+ : (23, 82). HNO_2 (aq) and NO_2^- : (23, 40); NO_3^- : ΔH (1, 28), S (28), C_p (46); $\text{H}_2\text{N}_2\text{O}_2$ (aq), HN_2O_2^- , N_2O_2^- : (40, 82); N_2O (aq) and NO (aq): (43); HCN (aq), CN^- , HCNO (aq), and CNO^- : (27); HCNS (aq) and CNS^- : (23, 40).

CO_2 (aq), H_2CO_3 (aq): (42, 43); HCO_3^- : (28, 42, 84) except C_p (45); CO_3^{\equiv} (28, 42, 85) except C_p (45); CO (aq): (43); H_2CO (aq): (23, 87); $\text{H}_2\text{C(OH)}_2$ (aq): (23, 27, 87); H_2COOH^- : (87); HCOOH (aq): (23, 27, 86, 88); HCOO^- : (23, 27); CH_3COOH (aq): ΔH and ΔS based on ionization data tabulated by Christensen et al. (86), C_p (77); CH_3COO^- : (40) except C_p (45, 77); $(\text{COOH})_2$ (aq): Based on ionization data (86); $\text{C}_2\text{O}_4^{\text{H}^-}$ and $\text{C}_2\text{O}_4^{\equiv}$: (40). $(\text{CH}_2)_2(\text{COOH})_2$ (aq): (89, 90); $(\text{CH}_2)_2(\text{COO})_2^{\text{H}^-}$ and $(\text{CH}_2)_2(\text{COO})_2^{\equiv}$: (86); $(\text{CH}_2)_4(\text{COOH})_2$ (aq): (89, 90, 91); $(\text{CH}_2)_4(\text{COO})_2^-$ and $(\text{CH}_2)_4(\text{COO})_2^{\equiv}$: (86).

Mn^{++} : (92, 93, 94); Mn^{+++} (82); Fe^{++} and Fe^{+++} : (95, 96), Mg^{++} : ΔH (97), S (29), C_p (45, 93, 98); Ca^{++} : (28), C_p (93, 98); Li^+ : (28), C_p (45); Na^+ : (28), C_p (46, 59); K^+ : (28), C_p (46).

TABLE IV Equations for $-(G^{\circ} - H_{298}^{\circ})/RT$ for 298.15K to T_{\max}

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
O(g)	1000	$20.151 - 7.110 \times 10^{-3} T + 1.9800 \times 10^{-5} T^2 - 1.816 \times 10^{-8} T^3 + 5.987 \times 10^{-12} T^4$	(8,9)
O_2 (g)	1000	$25.757 - 9.743 \times 10^{-3} T + 2.6812 \times 10^{-5} T^2 - 2.4157 \times 10^{-8} T^3 + 7.8845 \times 10^{-12} T^4$	(8,9)
O_3 (g)	1000	$30.370 - 1.4222 \times 10^{-2} T + 3.8373 \times 10^{-5} T^2 - 3.385 \times 10^{-8} T^3 + 1.0885 \times 10^{-11} T^4$	(8)
H(g)	6000	$11.284 + 2.5 [298.15/T - \ln(298.15/T)]$	(3)
H_2 (g)	1000	$16.784 - 9.639 \times 10^{-3} T + 2.6701 \times 10^{-5} T^2 - 2.436 \times 10^{-8} T^3 + 8.007 \times 10^{-12} T^4$	(8,9)
OH(g)	1000	$23.170 - 9.734 \times 10^{-3} T + 2.7076 \times 10^{-5} T^2 - 2.4774 \times 10^{-8} T^3 + 8.162 \times 10^{-12} T^4$	(8)
HO_2 (g)	1000	$28.909 - 1.2005 \times 10^{-2} T + 3.2678 \times 10^{-5} T^2 - 2.9068 \times 10^{-8} T^3 + 9.4155 \times 10^{-12} T^4$	(8,9)
H_2O (g)	1000	$23.939 - 1.1055 \times 10^{-2} T + 3.0494 \times 10^{-5} T^2 - 2.754 \times 10^{-8} T^3 + 9.016 \times 10^{-12} T^4$	(9)
H_2O_2 (g)	1000	$29.901 - 1.490 \times 10^{-2} T + 4.0313 \times 10^{-5} T^2 - 3.5592 \times 10^{-8} T^3 + 1.148 \times 10^{-11} T^4$	(8)
F(g)	1000	$19.906 - 7.426 \times 10^{-3} T + 2.070 \times 10^{-5} T^2 - 1.901 \times 10^{-8} T^3 + 6.269 \times 10^{-12} T^4$	(8)
F_2 (g)	1000	$25.601 - 1.0796 \times 10^{-2} T + 2.9565 \times 10^{-5} T^2 - 2.658 \times 10^{-8} T^3 + 8.651 \times 10^{-12} T^4$	(8)
HF(g)	1000	$21.961 - 9.604 \times 10^{-3} T + 2.6654 \times 10^{-5} T^2 - 2.4344 \times 10^{-8} T^3 + 8.008 \times 10^{-12} T^4$	(8)

Species	T _{max} , K	$-(G^\circ - H_{298}^\circ)/RT =$	Ref.
Cl(g)	1000	$20.695 - 7.4565 \times 10^{-3} T + 2.0567 \times 10^{-5} T^2 - 1.8693 \times 10^{-8} T^3 + 6.117 \times 10^{-12} T^4$	(8)
Cl ₂ (g)	1000	$28.130 - 1.1633 \times 10^{-2} T + 3.2008 \times 10^{-5} T^2 - 2.8973 \times 10^{-8} T^3 + 9.465 \times 10^{-12} T^4$	(8)
HCl(g)	1000	$23.535 - 9.568 \times 10^{-3} T + 2.6541 \times 10^{-5} T^2 - 2.421 \times 10^{-8} T^3 + 7.968 \times 10^{-12} T^4$	(8)
Br(g)	1000	$21.801 - 6.842 \times 10^{-3} T + 1.899 \times 10^{-5} T^2 - 1.7341 \times 10^{-8} T^3 + 5.703 \times 10^{-12} T^4$	(8)
Br ₂ (g)	1000	$30.867 - 1.2101 \times 10^{-2} T + 3.3458 \times 10^{-5} T^2 - 3.0435 \times 10^{-8} T^3 + 9.978 \times 10^{-12} T^4$	(8)
HBr(g)	1000	$24.950 - 9.534 \times 10^{-3} T + 2.6434 \times 10^{-5} T^2 - 2.407 \times 10^{-8} T^3 + 7.914 \times 10^{-12} T^4$	(8)
I(g)	1000	$19.230 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
I ₂ (g)	1000	$32.718 - 1.2287 \times 10^{-2} T + 3.4019 \times 10^{-5} T^2 - 3.0998 \times 10^{-8} T^3 + 1.0176 \times 10^{-11} T^4$	(8)
HI(g)	1000	$26.090 - 1.0922 \times 10^{-2} T + 2.9862 \times 10^{-5} T^2 - 2.7574 \times 10^{-8} T^3 + 9.204 \times 10^{-12} T^4$	(8)
S(g)	1000	$21.030 - 7.725 \times 10^{-3} T + 2.1563 \times 10^{-5} T^2 - 1.9851 \times 10^{-8} T^3 + 6.556 \times 10^{-12} T^4$	(8, 9)
S ₂ (g)	1000	$28.699 - 1.1222 \times 10^{-2} T + 3.0796 \times 10^{-5} T^2 - 2.7792 \times 10^{-8} T^3 + 9.067 \times 10^{-12} T^4$	(8, 9)
S ₃ (g)	1000	$33.068 - 4.357 \times 10^{-3} T + 1.3802 \times 10^{-5} T^2 - 6.464 \times 10^{-9} T^3$	(8)
S ₄ (g)	1000	$35.63 - 6.237 \times 10^{-3} T + 1.944 \times 10^{-5} T^2 - 9.065 \times 10^{-9} T^3$	(8)
S ₅ (g)	1000	$40.99 - 8.146 \times 10^{-3} T + 2.576 \times 10^{-5} T^2 - 1.207 \times 10^{-8} T^3$	(8)
S ₆ (g)	1000	$47.079 - 3.984 \times 10^{-2} T + 1.0898 \times 10^{-4} T^2 - 9.8128 \times 10^{-8} T^3 + 3.1944 \times 10^{-11} T^4$	(8)
S ₇ (g)	1000	$48.644 - 1.194 \times 10^{-2} T + 3.811 \times 10^{-5} T^2 - 1.791 \times 10^{-8} T^3$	(8)
S ₈ (g)	1000	$51.866 - 1.381 \times 10^{-2} T + 4.416 \times 10^{-5} T^2 - 2.0755 \times 10^{-8} T^3$	(8)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
HS(g)	1000	$24.670 - 1.0438 \times 10^{-2} T + 2.9134 \times 10^{-5} T^2 - 2.6763 \times 10^{-8} T^3 + 8.849 \times 10^{-12} T^4$	(8,9)
H ₂ S(g)	1000	$26.031 - 1.1458 \times 10^{-2} T + 3.1424 \times 10^{-5} T^2 - 2.8197 \times 10^{-8} T^3 + 9.207 \times 10^{-12} T^4$	(8,9)
SO(g)	1000	$27.844 - 1.0278 \times 10^{-2} T + 2.8161 \times 10^{-5} T^2 - 2.5297 \times 10^{-8} T^3 + 8.231 \times 10^{-12} T^4$	(8,9)
SO ₂ (g)	1000	$31.444 - 1.4018 \times 10^{-2} T + 3.8017 \times 10^{-5} T^2 - 3.370 \times 10^{-8} T^3 + 1.0875 \times 10^{-11} T^4$	(8)
SO ₃ (g)	1000	$32.988 - 1.8566 \times 10^{-2} T + 4.9875 \times 10^{-5} T^2 - 4.3737 \times 10^{-8} T^3 + 1.4012 \times 10^{-11} T^4$	(8)
S ₂ O(g)	1000	$33.876 - 1.5605 \times 10^{-2} T + 4.2477 \times 10^{-5} T^2 - 3.7926 \times 10^{-8} T^3 + 1.2285 \times 10^{-11} T^4$	(8)
H ₂ SO ₄ (g)	1000	$36.64 - 9.61 \times 10^{-3} T + 2.775 \times 10^{-5} T^2 - 1.25 \times 10^{-8} T^3$	(8,9)
N(g)	2000	$15.925 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
N ₂ (g)	1000	$24.0955 - 9.506 \times 10^{-3} T + 2.6323 \times 10^{-5} T^2 - 2.3912 \times 10^{-8} T^3 + 7.849 \times 10^{-12} T^4$	(8,9)
NH(g)	1000	$22.856 - 9.601 \times 10^{-3} T + 2.664 \times 10^{-5} T^2 - 2.4321 \times 10^{-8} T^3 + 8.006 \times 10^{-12} T^4$	(8)
NH ₂ (g)	1000	$24.703 + 1.1228 \times 10^{-2} T + 3.0891 \times 10^{-5} T^2 - 2.7835 \times 10^{-8} T^3 + 9.109 \times 10^{-12} T^4$	(8)
NH ₃ (g)	1000	$24.570 - 1.2236 \times 10^{-2} T + 3.3141 \times 10^{-5} T^2 - 2.9206 \times 10^{-8} T^3 + 9.436 \times 10^{-12} T^4$	(8)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
NO(g)	1000	$26.422 - 9.721 \times 10^{-3} T + 2.6892 \times 10^{-5} T^2 - 2.4384 \times 10^{-8} T^3 + 7.997 \times 10^{-12} T^4$	(8)
$NO_2(g)$	1000	$30.359 - 1.299 \times 10^{-2} T + 3.518 \times 10^{-5} T^2 - 3.109 \times 10^{-8} T^3 + 1.0026 \times 10^{-11} T^4$	(8)
$N_2O(g)$	1000	$28.028 - 1.378 \times 10^{-2} T + 3.7298 \times 10^{-5} T^2 - 3.3014 \times 10^{-8} T^3 + 1.0655 \times 10^{-11} T^4$	(8)
$N_2O_3(g)$	1000	$38.17 - 6.50 \times 10^{-3} T + 2.054 \times 10^{-5} T^2 - 9.474 \times 10^{-9} T^3$	(8)
$N_2O_4(g)$	1000	$39.99 - 2.927 \times 10^{-2} T + 7.86 \times 10^{-5} T^2 - 6.898 \times 10^{-8} T^3 + 2.212 \times 10^{-11} T^4$	(8)
$N_2O_5(g)$	1000	$43.42 - 9.960 \times 10^{-3} T + 2.970 \times 10^{-5} T^2 - 1.357 \times 10^{-8} T^3$	(8)
HNO(g)	1000	$27.831 - 1.126 \times 10^{-2} T + 3.077 \times 10^{-5} T^2 - 2.740 \times 10^{-8} T^3 + 8.903 \times 10^{-12} T^4$	(8)
$H_2NNO_2(g)$	1000	$32.87 - 7.224 \times 10^{-3} T + 1.994 \times 10^{-5} T^2 - 8.743 \times 10^{-9} T^3$	(8)
HONO(g)	1000	$30.86 - 4.853 \times 10^{-3} T + 1.441 \times 10^{-5} T^2 - 6.523 \times 10^{-9} T^3$	(8)
$HONO_2(g)$	1000	$34.517 - 2.077 \times 10^{-2} T + 5.519 \times 10^{-5} T^2 - 4.788 \times 10^{-8} T^3 + 1.5255 \times 10^{-11} T^4$	(8)
$HONH_2(g)$	1000	$28.77 - 5.215 \times 10^{-3} T + 1.504 \times 10^{-5} T^2 - 6.675 \times 10^{-9} T^3$	(8)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
C(g)	1000	$19.772 - 6.884 \times 10^{-3} T + 1.9091 \times 10^{-5} T^2 - 1.7432 \times 10^{-8} T^3 + 5.728 \times 10^{-12} T^4$	(9)
CO(g)	1000	$24.825 - 9.523 \times 10^{-3} T + 2.6363 \times 10^{-5} T^2 - 2.3935 \times 10^{-8} T^3 + 7.858 \times 10^{-12} T^4$	(9)
CO ₂ (g)	1000	$27.229 - 1.331 \times 10^{-2} T + 3.5974 \times 10^{-5} T^2 - 3.177 \times 10^{-8} T^3 + 1.024 \times 10^{-11} T^4$	(9)
CS(g)	1000	$26.455 - 1.0117 \times 10^{-2} T + 2.7736 \times 10^{-5} T^2 - 2.4947 \times 10^{-8} T^3 + 8.130 \times 10^{-12} T^4$	(9)
COS(g)	1000	$29.542 - 1.4862 \times 10^{-2} T + 4.029 \times 10^{-5} T^2 - 3.5768 \times 10^{-8} T^3 + 1.1556 \times 10^{-11} T^4$	(9)
CS ₂ (g)	1000	$30.460 - 1.6203 \times 10^{-2} T + 4.4067 \times 10^{-5} T^2 - 3.9307 \times 10^{-8} T^3 + 1.2733 \times 10^{-11} T^4$	(9)
CH ₄ (g)	1000	$23.829 - 1.243 \times 10^{-2} T + 3.3115 \times 10^{-5} T^2 - 2.841 \times 10^{-8} T^3 + 9.068 \times 10^{-12} T^4$	(9)
CH ₃ OH(g)	1000	$30.656 - 1.5764 \times 10^{-2} T + 4.151 \times 10^{-5} T^2 - 3.5265 \times 10^{-8} T^3 + 1.1145 \times 10^{-11} T^4$	(25)
CH ₂ O(g)	1000	$26.55 - 3.707 \times 10^{-3} T + 1.083 \times 10^{-5} T^2 - 4.76 \times 10^{-9} T^3$	(9)
HCOOH(g)	1000	$32.052 - 1.8039 \times 10^{-2} T + 4.7926 \times 10^{-5} T^2 - 4.1987 \times 10^{-8} T^3 + 1.370 \times 10^{-11} T^4$	(26)
(HCOOH) ₂ (g)	1000	$40.97 - 1.198 \times 10^{-2} T + 3.327 \times 10^{-5} T^2 - 1.45 \times 10^{-8} T^3$	(26)
Mg(g)	2000	$15.365 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
Ca(g)	1500	$16.115 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
Li(g)	1600	$14.178 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
Na(g)	1700	$15.975 + 2.5[298.15/T - \ln(298.15/T)]$	(3)
K(g)	1400	$16.771 + 2.5[298.15/T - \ln(298.15/T)]$	(3)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
$H_2O(l)$	500	$18.025 - 8.867 \times 10^{-2} T + 2.8856 \times 10^{-4} T^2 - 3.9505 \times 10^{-7} T^3 + 2.08 \times 10^{-10} T^4$	(9)
$Br_2(l)$	500	$22.845 - 3.628 \times 10^{-2} T + 8.841 \times 10^{-5} T^2 - 5.95 \times 10^{-8} T^3$	(8)
$I_2(s)$	387	$15.897 - 1.333 \times 10^{-2} T + 2.30 \times 10^{-5} T^2$	(8)
$I_2(l)$	760	$-45.946 + 1204.8/T + 9.569 \ln T$	(8)
$S(\text{ortho-rhombic})$	400	$4.50 - 4.58 \times 10^{-3} T + 8.11 \times 10^{-6} T^2$	(8, 9)
$S(\text{mono-clinic})$	400	$4.27 - 3.69 \times 10^{-3} T + 7.39 \times 10^{-6} T^2$	(8, 9)
$S(l)$	1000	$2.614 + 2.667 \times 10^{-3} T + 2.592 \times 10^{-6} T^2 - 1.67 \times 10^{-9} T^3$	(8)
$H_2SO_4(l)$	700	$23.435 - 3.773 \times 10^{-2} T + 8.96 \times 10^{-5} T^2 - 4.856 \times 10^{-8} T^3$	(9)
$HNO_3(l)$	350	$5.505 + 13.215 [298.15/T - \ln(298.15/T)]$	(27)
$NH_4NO_3(s)$	450	$21.94 - 2.623 \times 10^{-2} T + 4.086 \times 10^{-5} T^2 + 1.59 \times 10^{-8} T^3$	(8)
$NH_4NO_3(l)$	900	$-108.40 + 4468/T + 19.364 \ln T$	(8)
$NH_4Cl(s)$	500	$17.59 - 4.927 \times 10^{-2} T + 1.204 \times 10^{-4} T^2 - 8.27 \times 10^{-8} T^3$	(57)
$(NH_4)_2SO_4(s)$	600	$17.61 - 3.44 \times 10^{-2} T + 8.164 \times 10^{-5} T^2 - 4.86 \times 10^{-8} T^3$	(57)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
C(graphite)	1000	$1.125 - 3.593 \times 10^{-3} T + 9.165 \times 10^{-6} T^2 - 7.424 \times 10^{-9} T^3 + 2.249 \times 10^{-12} T^4$	(9)
Si(s)	1000	$3.095 - 7.270 \times 10^{-3} T + 1.976 \times 10^{-5} T^2 - 1.766 \times 10^{-8} T^3 + 5.73 \times 10^{-12} T^4$	(9)
$SiO_2(\alpha, \beta)$ quartz	1000	$6.94 - 1.682 \times 10^{-2} T + 4.48 \times 10^{-5} T^2 - 3.88 \times 10^{-8} T^3 + 1.236 \times 10^{-11} T^4$	(9)
$SiO_2(\alpha, \beta)$ crist.	1000	$7.60 - 1.975 \times 10^{-2} T + 5.146 \times 10^{-5} T^2 - 4.445 \times 10^{-8} T^3 + 1.396 \times 10^{-11} T^4$	(33)
Mg(s)	922	$4.88 - 8.405 \times 10^{-3} T + 2.308 \times 10^{-5} T^2 - 2.076 \times 10^{-8} T^3 + 6.80 \times 10^{-12} T^4$	(9)
MgO(s)	1000	$4.85 - 1.398 \times 10^{-2} T + 3.77 \times 10^{-5} T^2 - 3.342 \times 10^{-8} T^3 + 1.077 \times 10^{-11} T^4$	(9)
$Mg(OH)_2(s)$	600	$10.91 - 2.664 \times 10^{-2} T + 6.355 \times 10^{-5} T^2 - 3.85 \times 10^{-8} T^3$	(57)
$MgF_2(s)$	1000	$7.25 - 6.14 \times 10^{-3} T + 1.872 \times 10^{-5} T^2 - 8.66 \times 10^{-9} T^3$	(9)
$MgCl_2(s)$	990	$11.06 - 6.19 \times 10^{-3} T + 1.993 \times 10^{-5} T^2 - 9.34 \times 10^{-9} T^3$	(9)
$MgCl_2 \cdot 6H_2O(s)$	385	$44.03 + 1.3 \times 10^{-4} (T - 298.15)^2$	(41, 57)
$MgOHCl(s)$	850	$5.49 - 5.09 \times 10^{-3} T + 1.37 \times 10^{-5} T^2 + 6.6 \times 10^{-9} T^3$	(57)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
MgS(s)	1000	$6.22 - 3.83 \times 10^{-3} T + 1.248 \times 10^{-5} T^2 - 5.87 \times 10^{-9} T^3$	(9)
MgSO ₄ (s)	1000	$11.67 - 1.025 \times 10^{-2} T + 3.031 \times 10^{-5} T^2 - 1.367 \times 10^{-8} T^3$	(9)
MgSO ₄ ·H ₂ O(s)	320	$15.2 + 8 \times 10^{-5} (T - 298.15)^2$	(27)
MgSO ₄ ·6H ₂ O(s)	320	$41.9 + 1 \times 10^{-4} (T - 298.15)^2$	(57)
MgSO ₄ ·7H ₂ O(s)	320	$47.3 + 2 \times 10^{-4} (T - 298.15)^2$	(57)
MgCO ₃ (s)	1000	$9.05 - 1.228 \times 10^{-2} T + 3.172 \times 10^{-5} T^2 - 1.496 \times 10^{-8} T^3$	(9)
MgCO ₃ ·3H ₂ O(s)	320	$23.53 + 1 \times 10^{-4} (T - 298.15)^2$	(27)
Ca(s)	721	$5.49 - 4.67 \times 10^{-3} T + 1.20 \times 10^{-5} T^2 - 6.38 \times 10^{-9} T^3$	(9)
CaO(s)	1000	$4.82 - 4.07 \times 10^{-3} T + 1.26 \times 10^{-5} T^2 - 5.86 \times 10^{-9} T^3$	(9)
Ca(OH) ₂ (s)	1000	$13.73 - 3.24 \times 10^{-2} T + 8.79 \times 10^{-5} T^2 - 7.846 \times 10^{-8} T^3 + 2.544 \times 10^{-11} T^4$	(9)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
$\text{CaF}_2(s)$	1000	$10.97 - 2.416 \times 10^{-2} T + 6.62 \times 10^{-5} T^2 - 5.967 \times 10^{-8} T^3 + 1.95 \times 10^{-11} T^4$	(9)
$\text{CaCl}_2(s)$	1000	$15.39 - 2.49 \times 10^{-2} T + 6.862 \times 10^{-5} T^2 - 6.224 \times 10^{-8} T^3 + 2.04 \times 10^{-11} T^4$	(9)
$\text{CaS}(s)$	1000	$6.97 - 3.93 \times 10^{-3} T + 1.285 \times 10^{-5} T^2 - 6.05 \times 10^{-9} T^3$	(9)
$\text{CaSO}_3(s)$	1000	$12.75 - 9.16 \times 10^{-3} T + 2.75 \times 10^{-5} T^2 - 1.236 \times 10^{-8} T^3$	(36)
$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}(s)$	320	$14.7 + 7 \times 10^{-5} (T - 298.15)^2$	(37)
CaSO_4 (anhydride)	1000	$13.31 - 9.10 \times 10^{-3} T + 2.8245 \times 10^{-5} T^2 - 1.246 \times 10^{-8} T^3$	(38)
CaSO_4 (sol α)	320	$13.03 + 5.8 \times 10^{-5} (T - 298.15)^2$	(38)
CaSO_4 (sol β)	320	$13.03 + 5.7 \times 10^{-5} (T - 298.15)^2$	(38)
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(\alpha)$	450	$24.74 - 7.22 \times 10^{-2} T + 1.778 \times 10^{-4} T^2 - 1.253 \times 10^{-7} T^3$	(38)
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(\beta)$	450	$25.63 - 7.533 \times 10^{-2} T + 1.842 \times 10^{-4} T^2 - 1.28 \times 10^{-7} T^3$	(38)
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s)$	400	$29.31 - 4.183 \times 10^{-2} T + 7.30 \times 10^{-5} T^2$	(38)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
$\text{Ca}(\text{NO}_3)_2(s)$	800	$26.61 - 3.036 \times 10^{-2} T + 7.497 \times 10^{-5} T^2 - 3.77 \times 10^{-8} T^3$	(57)
CaCO_3 (calcite)	1000	$10.62 - 9.025 \times 10^{-3} T + 2.679 \times 10^{-5} T^2 - 1.221 \times 10^{-8} T^3$	(57)
$\text{Li}(s)$	454	$3.94 - 3.45 \times 10^{-3} T + 6.65 \times 10^{-6} T^2$	(10)
$\text{LiOH}(s)$	800	$6.35 - 1.06 \times 10^{-2} T + 2.60 \times 10^{-5} T^2 - 1.33 \times 10^{-8} T^3$	(9)
$\text{LiOH}\cdot\text{H}_2\text{O}(s)$	350	$8.61 + 5.1 \times 10^{-5} (T - 298.15)^2 - 1.6 \times 10^{-7} (T - 298.15)^3$	(57)
$\text{LiF}(s)$	1000	$4.55 - 4.06 \times 10^{-3} T + 1.25 \times 10^{-5} T^2 - 5.73 \times 10^{-9} T^3$	(9)
$\text{LiCl}(s)$	900	$7.67 - 6.29 \times 10^{-3} T + 1.73 \times 10^{-5} T^2 - 8.46 \times 10^{-9} T^3$	(9)
$\text{Li}_2\text{SO}_4(s)$	900	$15.53 - 1.863 \times 10^{-2} T + 4.831 \times 10^{-5} T^2 - 2.264 \times 10^{-8} T^3$	(9)
$\text{Na}(s)$	371	$6.17 + 1 \times 10^{-4} (T - 298.15) + 1.30 \times 10^{-5} (T - 298.15)^2$	(10)
$\text{NaOH}(s)$	600	$9.50 - 1.452 \times 10^{-2} T + 3.344 \times 10^{-5} T^2 - 1.619 \times 10^{-8} T^3$	(9)
$\text{NaF}(s)$	1000	$6.34 - 4.00 \times 10^{-3} T + 1.293 \times 10^{-5} T^2 - 6.03 \times 10^{-9} T^3$	(9)
$\text{NaCl}(s)$	1000	$8.83 - 4.09 \times 10^{-3} T + 1.346 \times 10^{-5} T^2 - 6.27 \times 10^{-9} T^3$	(9)
$\text{Na}_2\text{S}(s)$	1000	$11.81 - 6.48 \times 10^{-3} T + 2.167 \times 10^{-5} T^2 - 1.023 \times 10^{-8} T^3$	(9)
$\text{Na}_2\text{SO}_4(s)$	1000	$23.81 - 4.711 \times 10^{-2} T + 1.1182 \times 10^{-4} T^2 - 6.718 \times 10^{-8} T^3$	(9)
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	320	$71.15 + 3 \times 10^{-4} (T - 298.15)^2$	(57)

TABLE IV (CONTINUED)

Species	T_{\max}, K	$-(G^{\circ} - H_{298}^{\circ})/RT =$	Ref.
$NaNO_3(s)$	550	$15.10 - 1.026 \times 10^{-2} T + 2.165 \times 10^{-5} T^2$	(57)
$Na_2CO_3(s)$	900	$18.15 - 1.809 \times 10^{-2} T + 4.595 \times 10^{-5} T^2 - 2.151 \times 10^{-8} T^3$	(9)
$NaHCO_3(s)$	400	$15.17 - 1.985 \times 10^{-2} T + 3.46 \times 10^{-5} T^2$	(57)
$NaCHO_2(s)$	330	$12.48 + 5 \times 10^{-5} (T - 298.15)^2$	(40)
$K(s)$	336	$7.78 + 2 \times 10^{-5} (T - 298.15)^2$	(10)
$KF(s)$	1000	$8.175 - 4.07 \times 10^{-3} T + 1.327 \times 10^{-5} T^2 - 6.185 \times 10^{-9} T^3$	(9)
$KCl(s)$	1000	$10.14 - 4.17 \times 10^{-3} T + 1.37 \times 10^{-5} T^2 - 6.377 \times 10^{-9} T^3$	(9)
$K_2SO_4(s)$	900	$22.88 - 1.898 \times 10^{-2} T + 5.042 \times 10^{-5} T^2 - 2.392 \times 10^{-8} T^3$	(9)
$K_2S_4O_6(s)$	330	$37.24 - 4 \times 10^{-4} (T - 298.15) + 1.7 \times 10^{-4} (T - 298.15)^2 - 5 \times 10^{-7} (T - 298.15)^3$	(37)
$KNO_3(s)$	400	$19.60 - 2.47 \times 10^{-2} T + 4.22 \times 10^{-5} T^2$	(57)

Appendix: Calculator Program for Use of Tables I-IV

For the reaction $aA + bB = cC + dD$, the constants of Table IV for each of the reactants and products can be combined to yield an equation for $-\Delta(G^{\circ} - H_{298}^{\circ})/RT$ as a function of temperature. The $\Delta H_{298}^{\circ}/R$ values of Tables I-III can be combined to yield $\Delta H_{298}^{\circ}/R$ for the overall reaction.

$$\Delta H_{298}^{\circ}/R = d(\Delta H_{298}^{\circ}/R)_D + c(\Delta H_{298}^{\circ}/R)_C - b(\Delta H_{298}^{\circ}/R)_B - a(\Delta H_{298}^{\circ}/R)_A$$

The equilibrium constant can then be calculated by the equation

$$\ln K_T = -\Delta(G^{\circ} - H_{298}^{\circ})/RT - (\Delta H_{298}^{\circ}/R)/T$$

If $\ln K$ is known, the above equation can be used to calculate $\Delta H_{298}^{\circ}/R$. The following program will carry out these operations using the constants of Tables I-IV. HP41C programming is used.

Directions:

	<u>Display</u>
(1) $d \uparrow c \uparrow -b \uparrow -a$	XEQ 'AG'
	0

The sign is negative for each reactant coefficient and positive for each product coefficient. If the total of reactants and products is three, enter $d=0$. For $aA=cC$, enter $0 \uparrow 0 \uparrow c \uparrow -a$.

(2) $(a_0)_D \uparrow (a_0)_C \uparrow (a_0)_B \uparrow (a_0)_A$	User A	$d(a_0)_D$
$[(2')] e \text{ STO}9, (a_0)_E$	User e	$e(a_0)_E]$

$(2')$ is used only if the total of reactants and products is five. Step(2), and if necessary $(2')$, is repeated with a_1 values from Table IV, and then again with the a_2 values up to a_4 values if there are a_4 entries in Table IV for any of the reactants or products. If the sum of reactants and

products is three, no entries are made for D. Similarly, if there are only two species, no entry is needed of $(a_n)_B$ values. If there are only a_0 terms which correspond to the C_p/R values at 298K given in Tables I-III, no entries are made after the a_0 entries. However, if any reactant or product has a higher term, then entries, even when they are zero, are required through the highest a_n set with at least one non-zero value.

(3a) T_1 XEQ 1 $-\Delta(G^\circ - H_{298}^\circ)/RT_1$

(3b) (If I stored in R12) R/S $-\Delta(G^\circ - H_{298}^\circ)/RT$
for $T = T_1 + I$

(4) After 10.1 ST010, $\Delta H_{298}^\circ/R$ for each product and reactant is inserted as in (2), and if necessary (2').

(5a) To calculate average $\Delta H_{298}^\circ/R$ from a set of $\ln K_T$ values,
XEQ 5 to set up registers

$T \uparrow \ln K_T$ User H $\Delta H_{298}^\circ/R$

Repeat $T \uparrow \ln K_T$ for all T.

(5b) R/S, SST Av. $\Delta H_{298}^\circ/R$, Std. Dev.

(6a) After step 4 or 5 has stored $\Delta H_{298}^\circ/R$ in R11,

T_1 User E, SST $\ln K_{T_1}, K_{T_1}$

(6b) R/S, SST $\ln K_T, K_T$

for $T = T_1 + I$

Note 1: When $-(G^\circ - H_{298}^\circ)/RT$ is given as a function of $T - 298.15$, e.g. $a'_0 + a'_1(T - 298.15) + a'_2(T - 298.15)^2$, it is necessary to expand to obtain power series in T. In the example cited, $a_0 = a'_0 - 298.15a'_1 + a'_2(298.15)^2$ and $a_1 = a'_1 - 2(298.15)a'_2$.

Note 2: When the $-(G^\circ - H_{298}^\circ)/RT$ equation in Table IV contains $\ln T$ and T^{-1} terms, these terms should be entered by step (2) after insertion of the a_0 terms and before insertion of the a_1 terms. For an equation with $\ln T$, T^{-1} as well as T and T^2 terms, LBL 01 would be modified after RCL 02 of step 51 to

$R \uparrow / + R \uparrow \ln RCL 01 X + RCL 00 + RTN.$

PRP "AG"

R	00	1	2	3	4	5	6	7	8	9	10	Index	01+LBL "AG"
Δa_0	Δa_1	Δa_2	Δa_3	Δa_4	-a	-b	c	d	e	Δa		STO 05 RDN STO 06 RDN STO 07 RDN STO 08 -1.1 STO 10 0 STO 01 STO 02 STO 03 STO 04 STO 12 RTN	
11	12	13	14	15	18								
$\frac{\Delta H_{298}^\circ}{R}$	I	$\frac{\Sigma \Delta H_{298}^\circ}{R}$	$\Sigma \left(\frac{\Delta H_{298}^\circ}{R} \right)^2$	lnK	n								18+LBL A ISG 10 STO IND 10 CLX RCL 05 ST+ IND 10 RDN RCL 06 * ST+ IND 10 RDM RCL 07 * ST+ IND 10 RDM RCL 08 * ST+ IND 10 RTN
													37+LBL e RCL 09 * ST+ IND 10 RTN

SIZE 019, program has 94 steps using 124 bytes or 18 registers or a total of 37 registers needed. Program will set Σ registers starting at 13.

Test:

$\text{CaSO}_3(s) = \text{CaO}(s) + \text{SO}_2(g)$	XEQ 'AG'	42+LBL 01 ENTER↑ ENTER↑ ENTER↑ RCL 04 * RCL 03 + * RCL 02 + * RCL 01 + * RCL 00 + RTN RCL 12 R↑ + GTO 01
(1) 0 ↑ 1 ↑ 1 ↑ -1	User	
(2) 31.44 ↑ 4.82 ↑ 12.75	A	
$-1.4018 \times 10^{-2} \uparrow -4.07 \times 10^{-3} \uparrow -9.16 \times 10^{-3}$	A	64+LBL 05 ΣREG 13 CLE RTN
$3.8017 \times 10^{-5} \uparrow 1.26 \times 10^{-5} \uparrow 2.75 \times 10^{-5}$	A	
$-3.37 \times 10^{-8} \uparrow -5.86 \times 10^{-9} \uparrow -1.236 \times 10^{-8}$	A	68+LBL H STO 15 RDN XEQ 01 RCL 15 - R↑ * Σ+ LASTX RTN MEAN STO 11 RTN SDEV
$1.0875 \times 10^{-11} \uparrow 0 \uparrow 0$	A	
(3) EEX2 STO12, 800 XEQ1 21.694;		83+LBL E
(3b) R/S 21.510; R/S 21.378		XEQ 01 RCL 11 R↑ / - RTN E↑X RCL 12 R↑ + GTO E END
(4) 10.1 STO10, -35 700↑-76 380↑-139 400		
A 0; RCL11 27 320		
(6a) 800 E -12.456 SST 3.90×10^{-6}		
(5a) XEQ5, 800↑ -12.46 H 27 324	900↑ -8.85 H 27 324	
1000↑ -5.94 H 27 318	(5b) R/S 27 322, SST 3	

References

- (1) CODATA recommended key values for thermodynamics, 1977,
J. Chem. Thermodynamics 10, 903-6 (1978).
- (2) K.S. Pitzer, L. Brewer, J. Phys. Chem. Ref. Data 8,
917-9 (1979); High-Temp. Sci. 11, 49-53 (1979).
- (3) For the atomic gases H, the alkali and alkaline earth elements, N, Br, and I which have no significant contribution to the heat capacity other than translational between 0 and 298 K, $(H_{298}^0 - H_0^0)/R = (5/2)(298.1500) = 745.4$ K with no uncertainty. For the same atoms, the entropy can be calculated very accurately from Eq. 27-3 of ref.(4). Appendix 3 of ref.(4) derives Eqs. A3-15 and 16 which are given again as Eq. 27-2 from which 27-3 is derived. $S_{298}^0/R = 13.0791 + (3/2)\ln M + \ln g_e$. M is the atomic weight and g_e is the electronic degeneracy which is 1 for the alkaline earth elements, 2 for H and the alkali elements, and 4 for N, Br, and I. The constant $13.0791 = 5/2 + (3/2)\ln(2\pi/N_0 h^2) + (5/2)\ln k - \ln 1013250$. The values used were $N_0 = 6.02209 \times 10^{23}$, $h = 6.62618 \times 10^{27}$ erg sec, and $k = 1.38065 \times 10^{-16}$ erg K^{-1} (5,6). The error in S_{298}^0/R due to uncertainties in the constants and atomic weights (7) or the use of an average molecular weight for an isotopic mixture is 0.001 or smaller for all of these elements. The values calculated here agree with the CODATA values(1) within rounding errors, but their uncer-

References (continued)

- tainties are too high.
- (4) G.N. Lewis, M. Randall, K.S. Pitzer, L. Brewer,
Thermodynamics, 2nd Ed., McGraw-Hill Book Co., New York
(1961).
- (5) E.R. Cohen, B.N. Taylor, J. Phys. Chem. Ref. Data 2,
663-734 (1973).
- (6) B.N. Taylor, E.R. Cohen in Atomic Masses and Fundamental
Constants, Proc. 5th Int. Conf., 1975, Eds. J.H. Sanders,
A.H. Wapstra, Plenum Press, New York (1976).
- (7) Commision on Atomic Weights, Inorganic Chemistry Division
of IUPAC, Atomic weights of the elements 1975, Pure
Appl. Chem. 47, 75-95 (1976).
- (8) V.P. Glushko, V.V. Gurvich, G.A. Bergman, I.V. Veitz,
V.A. Medvedev, G.A. Khachkurov, V.S. Yungman, Thermo-
dynamic Properties of Individual Substances, High-Tempera-
ture Institute, State Institute of Applied Chemistry,
National Academy of Sciences of the U.S.S.R., Moscow
(1978). Vol. 1: Compounds of O, H, F, Cl, Br, I, He, Ne,
Ar, Kr, Rn, S, N, and P.
- (9) M.W. Chase, Jr., J.L. Curnutt, R.A. McDonald, A.N. Syverud,
JANAF Thermochemical Tables, 1978 Supplement, J. Phys.
Chem. Ref. Data 7, 793-940 (1978) and additional supple-
ments.
- (10) R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K.

References (continued)

- Kelley, and D.D. Wagman, Selected Values of the Thermo-dynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio (1973).
- (11) The CODATA enthalpy of formation values(1) for Br and I were slightly revised to correspond to the values reported by R.F. Barrow, D.F. Broyd, L.V. Pederson, K.K. Yee, Chem. Phys. Letters 18, 357 (1973).
- (12) G.K. Johnson, J. Chem. Thermodynamics 9, 835-41 (1977).
- (13) The CODATA ΔH value for S(g) was changed in acknowledgement of the objection raised by K.P. Huber and G. Herzberg (14) and to be consistent with the value selected(10) for S₂(g).
- (14) K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV: Constants of Diatomic Molecules. Van Nostrand Reinhold, New York, 1979.
- (15) R. Steudel and F. Schuster, J. Mol. Struct. 44, 143-57 (1978).
- (16) H. Rau, T.R.N. Kutty, J.R.F. Guedes De Carvalho, J. Chem. Thermodynamics 5, 833-44 (1973).
- (17) D. Detry, J. Drowart, P. Goldfinger, H. Keller, H. Rickert, Z. Phys. Chem. N.F. 55, 314-9 (1967).
- (18) T. Rosenquist, J. Haugom, J.C.S. Faraday I 73, 913-9 (1977).
- (19) F.J. Lovas, J. Phys. Chem. Ref. Data 7, 1445 (1978).
- (20) S.W. Benson, Chem. Rev. 78, 23-35 (1978).

References (continued)

- (21) L.G. Piper, J. Chem. Phys. 70, 3417-9 (1979).
- (22) J. Drowart, J. Smets, J.C. Reynaert, P. Coppens, Adv. Mass Spect. 7A, 647-50 (1978).
- (23) D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, R.H. Schumm, Nat. Bur. Stand. U.S. Technical Note 270-3 (1968).
- (24) E.S. Domalski, J. Phys. Chem. Ref. Data 1, 221-77 (1972).
- (25) S.S. Chen, R.C. Wilhoit, B.J. Zwolinski, J. Phys. Chem. Ref. Data 6, 105-112 (1977).
- (26) J. Chao, B.J. Zwolinski, J. Phys. Chem. Ref. Data 7, 363-77 (1978).
- (27) V.P. Clushkov, V.A. Medvedev, V.S. Yungman, G.A. Bergman, V.P. Kolesov, L.V. Gurvich, A.F. Vorob'yev, V.P. Vasil'yev, V.N. Kostryukov, L.A. Reznitskii, N.T. Ioffe, et. al. Thermodynamic Constants of Materials, All Union Institute of Scientific and Technical Information (VINITI), Institute for High Temperature, Vol. II S, Se, Te, Po (1966), Vol. IV C, Si, Ge, Sn, Pb (1970), Vol. IX Be, Mg, Cu, Sr, Ba, Ra (1979).
- (28) D.D. Wagman, U.S. National Bureau of Standards, private communication, June 1980, of proposed modifications of CODATA values (1). To be consistent with these changes, appropriate corrections have been applied to values taken from earlier tabulations when the accuracy of the data

References (continued)

- warranted the small corrections.
- (29) V.B. Parker, D.D. Wagman, W.H. Evans, Nat. Bur. Stand. U.S. Technical Note 270-6 (1971).
- (30) Wagman (28) has listed values from references cited in CODATA Bulletin No. 10, 1973 as being the best data available up to June 1980.
- (31) G.A. Nash, H.A. Skinner, T.A. Zordan, and L.G. Hepler, J. Chem. Eng. Data 13, 271-2 (1968).
- (32) A. Navrotsky, Arizona State University, private communication, Aug. 1980, of determination of enthalpy difference of quartz and cristobalite.
- (33) The JANAF values (9) for cristobalite were revised using the measurements of A.J. Leadbetter and T.W. Smith, Phil. Mag. 33, 113-9 (1976).
- (34) C. Shin, C.M. Criss, J. Chem. Thermodynamics 11, 663-6 (1979).
- (35) B.S. Hemingway and R.A. Robie, J. Res. U.S. Geol. Surv. 1(5), 535-41, 543-7 (1973).
- (36) D. Cubicciotti, A. Sanjuyo, and D.L. Hildenbrand, J. Electrochem. Soc. 124, 933-6 (1977).
- (37) The calculations of J.W. Cobble, H.P. Stephens, I.R. McKinnon, E.F. Westrum, Jr., Inorg. Chem. 11, 1669-74 (1972) have been corrected to be consistent with the values of Table III.

References (continued)

- (38) K.K. Kelley, J.C. Southard, C.T. Anderson, U.S. Bur. Mines Tech. Paper 625 (1941). All of their $\Delta H/R$ values were made 2040K more negative to be consistent with values for $SO_4^{=}$ and Ca^{++} of Table III and the values for $CaSO_4$ (anhydrite) and $CaSO_4 \cdot 2H_2O(s)$ recommended by Wagman (28).
- (39) L.A.K. Staveley and R.G. Linford. J. Chem. Thermodynamics 1, 1-11 (1969).
- (40) D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, R.L. Nuttall, Nat. Bur. of Standards Technical Note 270-8 (1981).
- (41) K.K. Kelley, E.G. King, U.S. Bur. Mines Bull. 592 (1961).
- (42) R.L. Berg and C.E. Vanderzee, J. Chem. Thermodynamics 10, 1113-36 (1978).
- (43) E. Wilhelm, R. Battino, R.J. Wilcox, Chem. Rev. 77, 219-62 (1977).
- (44) O. Enea, P.P. Singh, E.M. Woolley, K.G. McCurdy, L.G. Hepler, J. Chem. Thermodynamics 9, 731-4 (1977).
- (45) J.E. Desnoyers, C. de Visser, G. Perron, P. Picker, J. Solution Chem. 5, 605-16 (1976).
- (46) A. Roux, G.M. Musbally, G. Perron, J.E. Desnoyers, P.P. Singh, E.M. Woolley, L.G. Hepler, Can. J. Chem. 56, 24-8 (1978).
- (47) C. Wu, M.M. Berky, L.G. Hepler, J. Phys. Chem. 67, 1202-5 (1963).

References (continued)

- (48) V.P. Vasil'ev, E.V. Kozlovskii, B.T. Kunin, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Teknol. 16(3), 365-8 (1973).
- (49) P.P. Singh, E.M. Woolley, K.G. McCurdy, L.G. Hepler, Can. J. Chem. 54, 3315-8 (1976).
- (50) R.W. Ramette, R.W. Sandford, Jr., J. Am. Chem. Soc. 87, 5001-5 (1965).
- (51) H.C. Helgeson, J. Phys. Chem. 71, 3121-36 (1967).
- (52) T.J. Edwards, G. Maurer, J. Newman, J.M. Prausnitz, AIChE Journal 24, 966-76 (1978).
- (53) CODATA Special Report, Part VIII, April, 1980.
- (54) C. Tsonopoulos, D.M. Coulson, and L.B. Inman, J. Chem. Eng. Data 21, 190-3 (1976).
- (55) J. Jordan, U.S. Dept. of Energy, Div. of Fossil Energy, Report FE-2710-1, pg. 24 (Jan. 1978) and FE-2710-3, p. 11, 17 (July 1978).
- (56) W. Giggenbach, Inorg. Chem. 10, 1333-8 (1971).
- (57) K.K. Kelley, Bureau of Mines Bulletin 584, U.S. Govt. Printing Office, Washington, D.C. (1960).
- (58) A.C. MacLeod, Trans. Far. Soc. I69, 2026-35 (1973).
- (59) G.C. Allred, E.M. Woolley, J. Chem. Thermodynamics 13, 147-54 (1981).
- (60) B. Meyer and L. Peter, private communication, March 1981.
- (61) G. Schwarzenbach and A. Fischer, Helv. Chim. Acta 43, 1365-90 (1960).
- (62) G. Maronny, J. chim. phys. et phys.-chim. biol., 56(2), 202-21 (1959).

References (continued)

- (63) A. Huss, Jr., C.A. Eckert, J. Phys. Chem. 81, 2268-70 (1977).
- (64) R.E. Connick, T.M. Tam, E.V. Deuster, LBL-12272 (1981).
- (65) K.S. Pitzer, R.N. Roy, L.F. Silvester, J. Am. Chem. Soc. 99, 4930-6 (1977).
- (66) G.E.K. Branch, M. Calvin, *The Theory of Organic Chemistry*, Prentice-Hall, 1941.
- (67) J.H. Baxendale, M.D. Ward, P. Wardman, Trans. Faraday Soc. 67, 2532-7 (1971).
- (68) E. Hayon, A. Treinin, J. Wilf, J. Am. Chem. Soc. 94, 47-57 (1972).
- (69) I. Olofsson and S. Sunner, J. Chem. Thermodynamics 11, 605-11 (1979) and references cited therein.
- (70) P.R. Tremaine, S. Goldman, J. Phys. Chem. 82, 2317-21 (1978).
- (71) F.M. Page, J. Chem. Soc. 1953, 1719-24.
- (72) J. Boulegue, G. Michard, J. Fr. Hydrol. 9(1), 27-33 (1978).
- (73) G. Olofsson, J.J. Spitzer, L.G. Hepler, Can. J. Chem. 56, 1871-3 (1978).
- (74) W.L. Gardner, E.C. Jekel, J.W. Cobble, J. Phys. Chem. 73, 2017-20 (1969).
- (75) P.S.Z. Rogers, K.S. Pitzer, LBL-12415 (March 1981).
- (76) H.C. Ko, G.E. Daut, Bur. Mines Report of Investigations RI 8409, 8 pg. (1980).
- (77) G.C. Allred, E.M. Woolley, J. Chem. Thermodynamics 13, 155-64 (1981).
- (78) G. Olofsson, J. Chem. Thermodynamics 7, 507-14 (1975).

References (continued)

- (79) C.E. Vanderzee, D.L. King, *J. Chem. Thermodynamics* 4, 675-83 (1972).
- (80) C.E. Vanderzee, D.L. King, I. Wadsö, *J. Chem. Thermodynamics* 4, 685-9 (1972).
- (81) G. Olofsson, *J. Chem. Thermodynamics* 7, 507-14 (1975).
- (82) W.M. Latimer, *Oxidation Potentials*, 2nd Ed., Prentice-Hall, N.Y., 1952.
- (83) R.T.M. Fraser, *J. Chem. Soc.* 1965, 1747-9.
- (84) K.S. Pitzer, J.C. Peiper, *J. Phys. Chem.* 84, 2396-8 (1980).
- (85) J.C. Peiper, K.S. Pitzer, "Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate and Chloride," LBL-12725 (1981).
- (86) J.J. Christensen, L.D. Hansen, R.M. Izatt, *Handbook of Proton Ionization Heats and Related Thermodynamic Quantities*, John Wiley, N.Y. (1976).
- (87) B. Meyer, *Urea-Formaldehyde Resins*, pp. 26, 27, 31, Addison-Wesley, Reading, Massachusetts, 1979.
- (88) Th. Ackermann, F. Schreiner, *Z. Electrochemie*, 62, 1143-51 (1958).
- (89) J.B. Pedley, J. Rylance, *Sussex-N.P.L. Computer Analysed Thermodynamic Data: Organic and Organometallic Compounds*, Sussex Univ., 1977.
- (90) N. Nichols, R. Sköld, C. Spink, I. Wadsö, *J. Chem. Thermodynamics* 8, 993-9 (1976).
- (91) M. Davies, D.M.L. Griffiths, *Trans. Far. Soc.* 49, 1405-10 (1953).

References (continued)

- (92) L.M. Gedansky, L.G. Hepler, Can. J. Chem. 47, 699-701 (1969).
- (93) J.J. Spitzer, I.V. Olofsson, P.P. Singh, L.G. Hepler, J. Chem. Thermodynamics 11, 233-8 (1979).
- (94) J.J. Spitzer, I.V. Olofsson, P.P. Singh, L.G. Hepler, Thermochim. Acta 28, 155-60 (1979).
- (95) D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, and R.H. Schumm, Nat. Bur. Stand. U.S. Technical Note 270-4 (1969).
- (96) E.E. Bernarducci, L.R. Morss, A.R. Mikeztal, J. Soln. Chem. 8, 717-27 (1979).
- (97) G. Coffy, G. Olofsson, J. Chem. Thermodynamics 11, 141-44 (1979).
- (98) J.J. Spitzer, P.P. Singh, K.G. McCurdy, L.G. Hepler, J. Soln. Chem. 7, 81-6 (1978).

